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EFFECT OF ADDITIVES ON THERMAL STABILITY OF TUNGSTEN - URANIUM DIOXIDE COMPOSITES [U]

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Cleveland, Ohio

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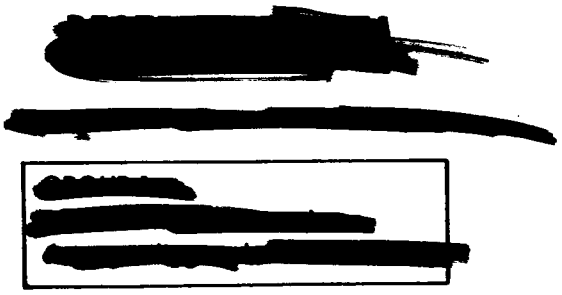

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EFFECT OF ADDITIVES ON THERMAL STABILITY OF TUNGSTEN - URANIUM DIOXIDE COMPOSITES (U)

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SUMMARY

Binary solid solutions of uranium dioxide with calcium oxide, zirconium dioxide, and thorium dioxide were prepared by sintering blended powders. Tungsten - uranium dioxide composites were fabricated with and without the solid-solution additions and were subjected to cyclic heating at 2500° C under flowing hydrogen. Under such conditions, composites containing uranium dioxide with additives in solid solution showed lower weight losses than composites without additives.

The effect of calcium oxide on the stability of the composites was significantly better than that of zirconium dioxide or thorium dioxide. This stability was probably due to the vacancy defect structure of the uranium dioxide - calcium oxide solid solution, which was less susceptible to oxygen loss than the nonvacancy structures of the uranium dioxide - zirconium dioxide and the uranium dioxide - thorium dioxide solid solutions.

The effect of thorium dioxide additions directly to the matrix was investigated and was found to be approximately the same as the effect of thorium dioxide in solid solution on the fuel-retention properties of the composites. Matrix additions of thorium dioxide did, however, contribute to the stability of the calcium oxide containing composites.

INTRODUCTION

Composites consisting of uranium dioxide dispersed in a tungsten matrix show poor fuel-retention properties at elevated temperatures under reducing conditions. These properties would severely limit their application in high-temperature nuclear-rocket reactors. Although uranium dioxide is generally nonreactive with the matrix metal, significant loss of the fuel from the composites has been observed during heating above 2200° C in flowing hydrogen. Furthermore, thermal cycling, which would be required of these composites if they were used as fuel elements in nuclear reactor applications, aggravates this condition (ref. 1).

The loss of oxide is generally thought to be caused by vaporization and diffusion through microcracks in the matrix that interconnect oxide particles with the surface. Although this process probably accounts for an appreciable loss of oxide because of the high vapor pressure of uranium dioxide (ref. 2, p. 197), the appearance of free uranium metal in the matrix (ref. 3) suggests that a more complex process also occurs.

Means of minimizing fuel loss under cyclic heating conditions have included coating fuel particles, controlling fuel particle size, controlling atmosphere, and adding stable oxides to the matrix. Because the composition of the oxide itself may have a significant effect on stability, research has been undertaken to ascertain the effect of solid-solution additions to uranium dioxide.

The additives studied were calcium oxide, zirconium dioxide, and thorium dioxide. These particular oxides were chosen because (1) their phase relations to uranium dioxide are known, (2) they form solid solutions with uranium dioxide, (3) small additions do not drastically lower the melting temperature of uranium dioxide, and (4) their nuclear properties are compatible with the projected use of the composites.

Also reported herein is the effect of the addition of thorium dioxide to the matrix; the purpose of this addition was to ascertain whether the beneficial effects reported in reference 1 were additive to uranium dioxide solid-solution effects.

EXPERIMENTAL PROCEDURE

Materials

The chemical analyses of uranium dioxide (UO_2) and additive powders are listed in table I. Ceramic grade UO_2 was used because of the fine particle size available. This material had an oxygen-uranium ratio (O/U) of 2.22 and contained the naturally occurring proportions of uranium 235 to uranium 238.

Preparation of Solid Solutions

Three 200-gram lots of UO_2 were prepared, each containing a different additive to the extent of 10 atomic percent. Lots without additives were also prepared. The powders were dry blended for 4 hours in a stainless-steel V-blender. Pressing was accomplished within a cylindrical rubber mold under a hydrostatic pressure of approximately 5.3×10^8 newtons per square meter (approx 75 000 lb/sq in.). The pressed cylinders were 5.5 centimeters long and 3.75 centimeters in diameter.

These compacts were sintered at 2200° C within a closed tungsten (W) crucible in a

TABLE I. - CHEMICAL ANALYSIS AND PARTICLE SIZE OF OXIDE POWDERS USED

Element or group	Powder			
	UO_2	CaO	ZrO_2	ThO_2
	Fisher size, μ			
	0.49	3.01	6.80	0.58
	Amount present, ppm			
Fe	<20	300	3000	<20
B	<.2	(a)	(a)	<.5
Co	<5	(a)	(a)	<5
Cd	<.5	(a)	(a)	<.5
Mn	<10	30	30	<10
Al	<20	1500	2000	<20
Mg	<10	3000	7000	<10
Zn	(a)	(a)	(a)	<20
Sn	<2	(a)	(a)	<2
Cu	<6	(a)	(a)	<6
Pb	<2	30	(a)	<2
Cr	<10	10	(a)	<10
Si	<25	5000	6200	<50
Ti	<10	30	660	<10
Ni	<10	(a)	(a)	<10
Mo	4	(a)	(a)	<10
V	<1	(a)	(a)	<1
Ca	<25	(a)	4800	<10
Be	<10	(a)	(a)	<1
Zr	<10	10	(a)	(a)
Na	<20	100	10	<20
P	(a)	(a)	(a)	<5
S	(a)	(a)	(a)	<10
C	<64	(a)	(a)	143
F	39	(a)	(a)	10
Cl	(a)	2	(a)	13
NO	(a)	<500	(a)	(a)
SO_4	(a)	<400	(a)	(a)

[a]None detected.

zirconium dioxide (ZrO_2) insulated tungsten tube furnace that was resistance heated. A center hole in the crucible cover facilitated temperature measurements with an optical pyrometer under conditions approximating those for a blackbody. The optical pyrometer used was calibrated for the sight glass and prism of the optical system by means of a standard lamp, calibration of which was traceable to the National Bureau of Standards.

Figure 1 illustrates the heating cycle used for sintering. The 1/2-hour hold at 1100° C under hydrogen was used to remove excess oxygen (O/U = 2.22) before sintering sealed the surface pores.

Solid solutions of thorium dioxide (ThO_2) in UO_2 have been successfully prepared by air sintering at 1650° C for 18 hours (ref. 4). In this investigation, the sintering cycle for the UO_2 solid solutions included a 6-hour hold at 2200° C. As can be seen from the phase diagram of figure 2(a), sintering at 2200° C permits liquid-state sintering of the calcium oxide (CaO) containing material (ref. 5). The liquid is consumed as diffusion progresses. This process will not occur in the case of ZrO_2 or ThO_2 (figs. 2(b) and (c)). The solid-solution compacts will be designated herein as UO_2:M, where M is either CaO, ZrO_2, or ThO_2, and will indicate a nominal composition of 10 atomic percent additive.

After sintering, a small sample was chipped off each solid-solution compact for metallographic inspection. The specimens were mounted in epoxy and ground

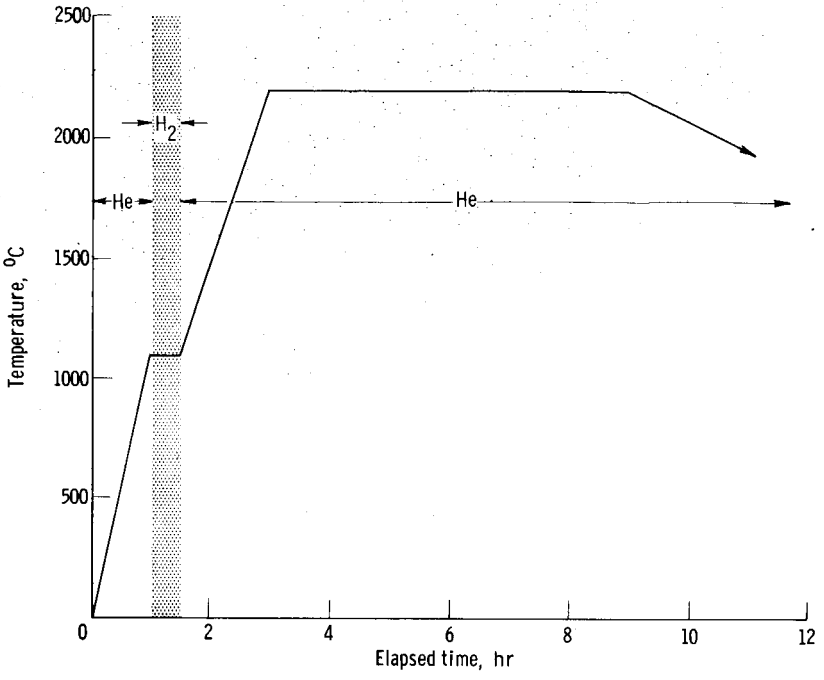


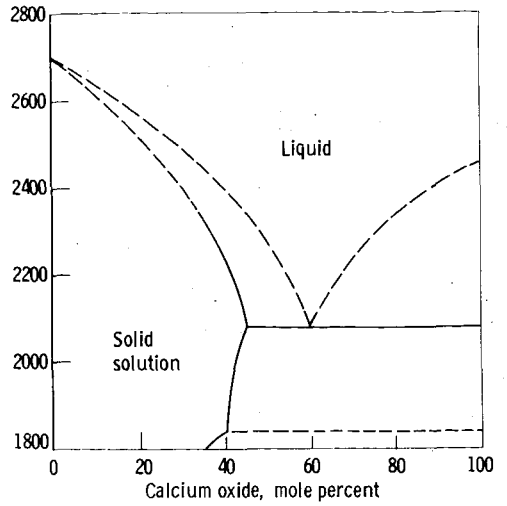
Figure 1. - Sintering and diffusion cycle for preparation of oxide - uranium dioxide solid solutions.

TABLE II. - COMPOSITION, LATTICE PARAMETERS, AND HARDNESSES OF OXIDES USED

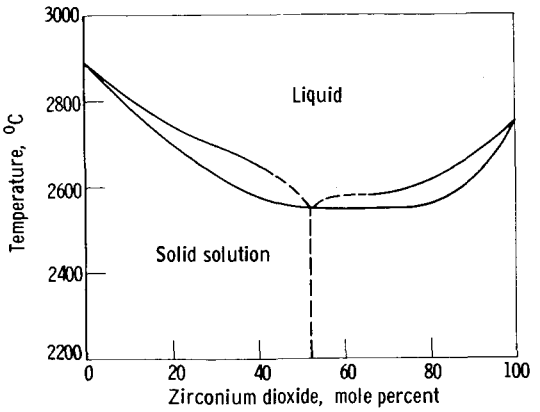
Oxide	Analysis for oxide additions		Calculated anion-to-cation ratio	Lattice parameter, Å	Vickers hardness number (100 g)
	Weight percent	Atomic percent			
UO_2	----	----	----	5.4678	1105
UO_2:CaO	2.15	9.61	1.90	5.4514	860
UO_2:ZrO_2	6.08	12.4	2.00	5.4322	1085
UO_2:ThO_2	9.93	10.2	2.00	5.4810	940

flat on 240-, 400-, and 600-grit silicon carbide paper. Rough polishing was done on silk with 6-micron diamond and on Pellon with 0.3-micron alumina. The microstructures of the compacts are discussed in the appendix.

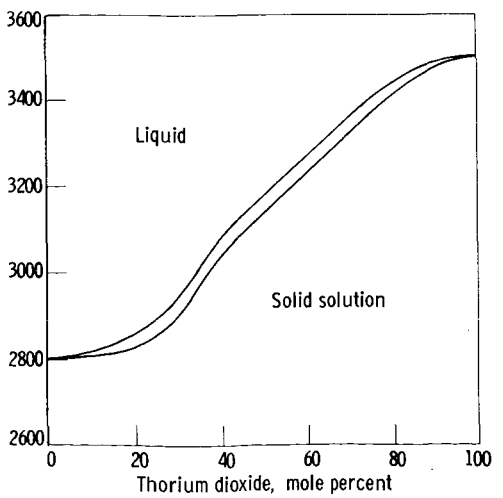
The solid solutions were chemically analyzed for the additive elements (table II). Also listed in table II are the lattice parameters of the solid solutions and their Vickers



(a) Uranium dioxide - calcium oxide.



(b) Uranium dioxide - zirconium dioxide.



(c) Uranium dioxide - thorium dioxide.

Figure 2. - Phase equilibrium diagrams (from ref. 5).

hardnesses. Each of the hardnesses listed is the average of 10 readings. The solid-solution compacts were crushed between tungsten plates and screened into two portions: -270+400 mesh and -400 mesh.

Preparation of Composites

Composites were fabricated from both the -270+400 and the -400 mesh fractions of solid-solution powders by the method used by Watson (ref. 6). The oxide powders were blended with 0.88-micron tungsten powder for 4 hours in a stainless-steel V-blender with stearic acid and acetone. Each composite contained the equivalent of 12.4 weight percent UO_2. This figure was obtained from possible application requirements. Composites were also made with 1.2 weight percent ThO_2 blended with the tungsten and oxide powders.

The powders were compacted in a steel die at 1.4×10^8 newtons per square meter (20 000 lb/sq in.). The composites were sintered in hy-

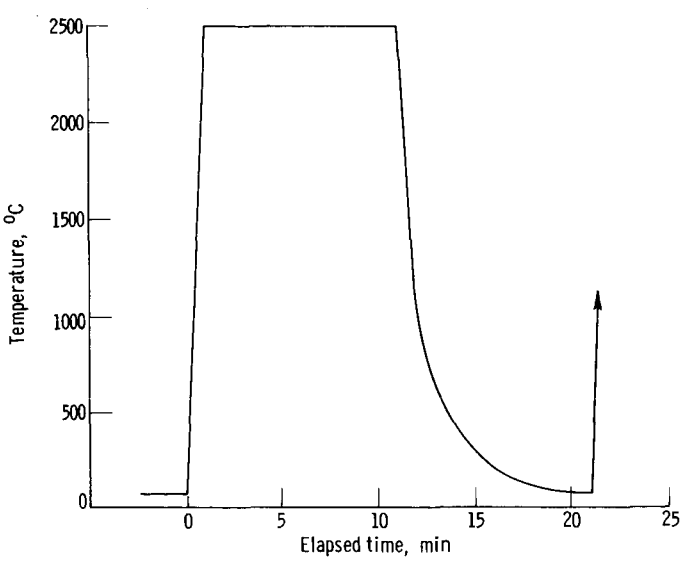
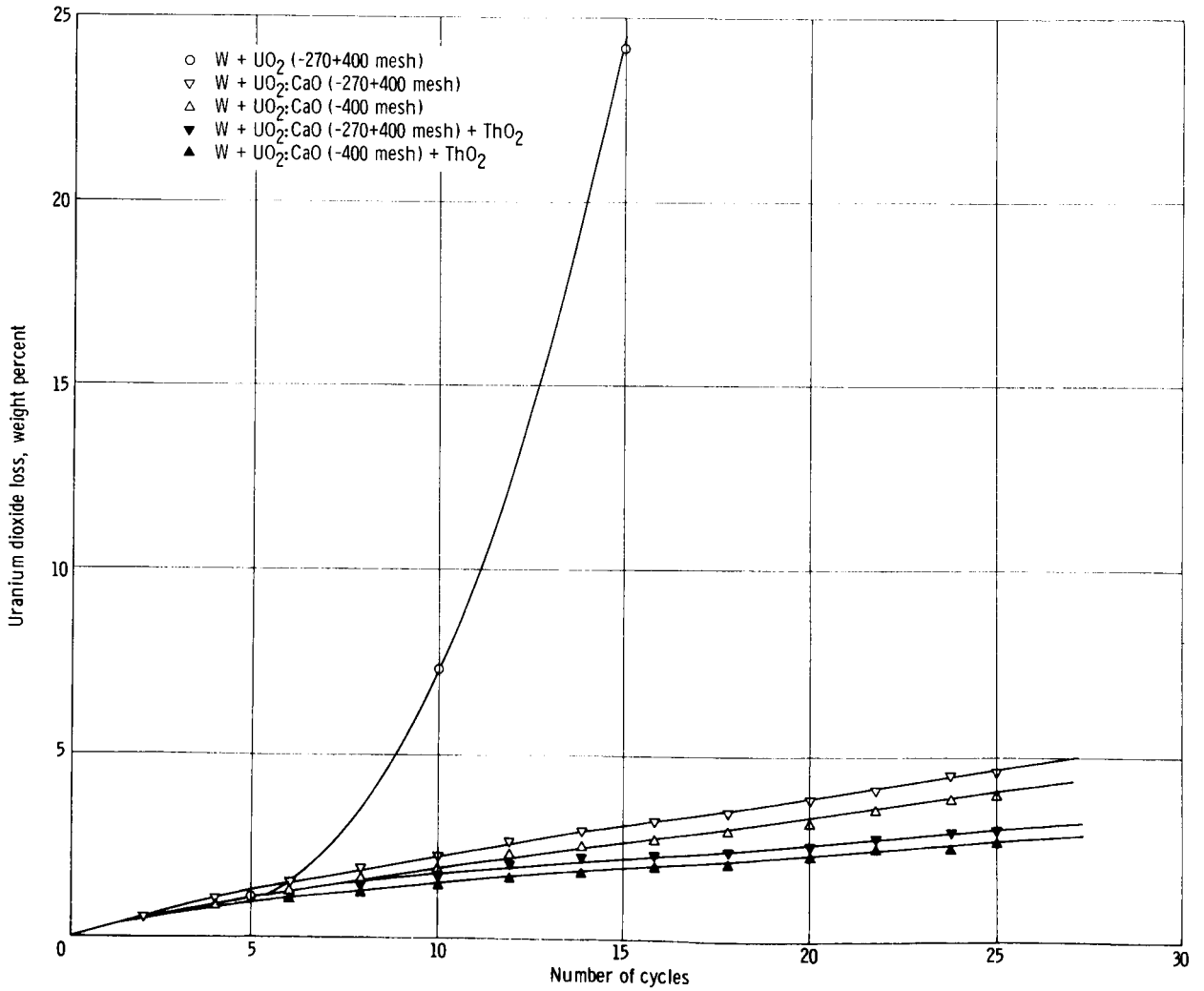


Figure 3. - Thermal cycle for fuel-loss determination.

drogen at 1750° C for 15 hours and then surface-ground to a thickness of 0.076 centimeter. The plates were then roll-clad at 1950° C under hydrogen with a 0.0076-centimeter tungsten foil on both major surfaces. Rolling reduced the total thickness (core and clad) to 0.053 centimeter. The plates were cut into coupons 3.5 by 2.5 centimeters. The edges were not clad. Before and after the cycling runs, samples of composites were sectioned and mounted in epoxy for metallographic examination of the cross section. The cut surface was ground on 240-, 400-, and 600-grit silicon carbide paper and rough-polished on nylon with 0.3-micron alumina and final-polished on Gamal with the same abrasive.

Stability Tests

Stability tests were conducted in an induction-heated furnace with a tungsten susceptor



(a) Composites containing calcium oxide.

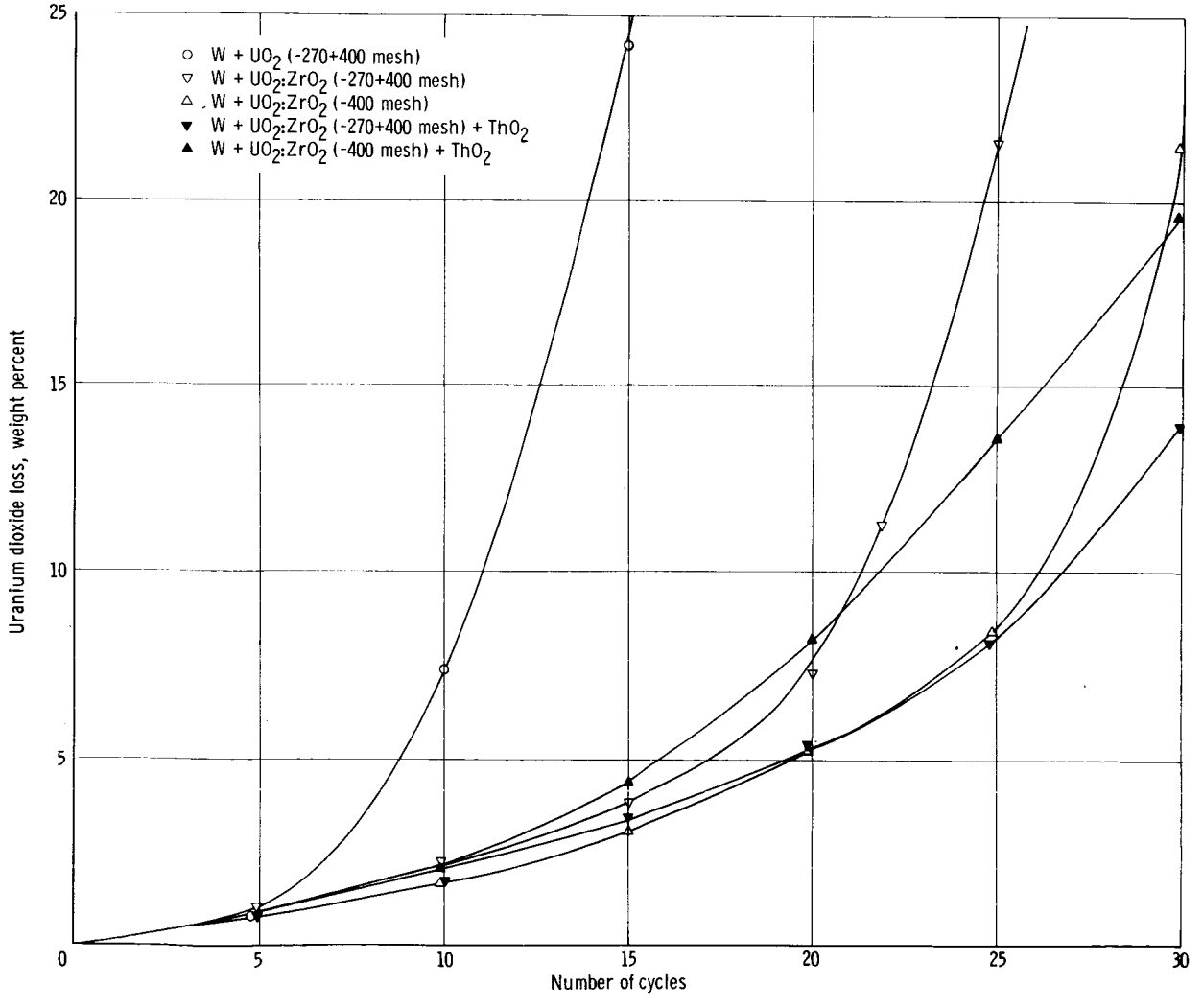
Figure 4. - Thermal stability of various composites.

under hydrogen flowing at 0.25 liter per second at atmospheric pressure. The coupons were so spaced that the gas could flow freely about them during thermal cycling. (Fig. 3 represents schematically a thermal cycle.) Blackbody temperatures were measured with an optical pyrometer; corrections were made for the sight glass and prism used in the optical system. A run consisted of at least 25 cycles; weight measurements were made at least every five cycles.

RESULTS

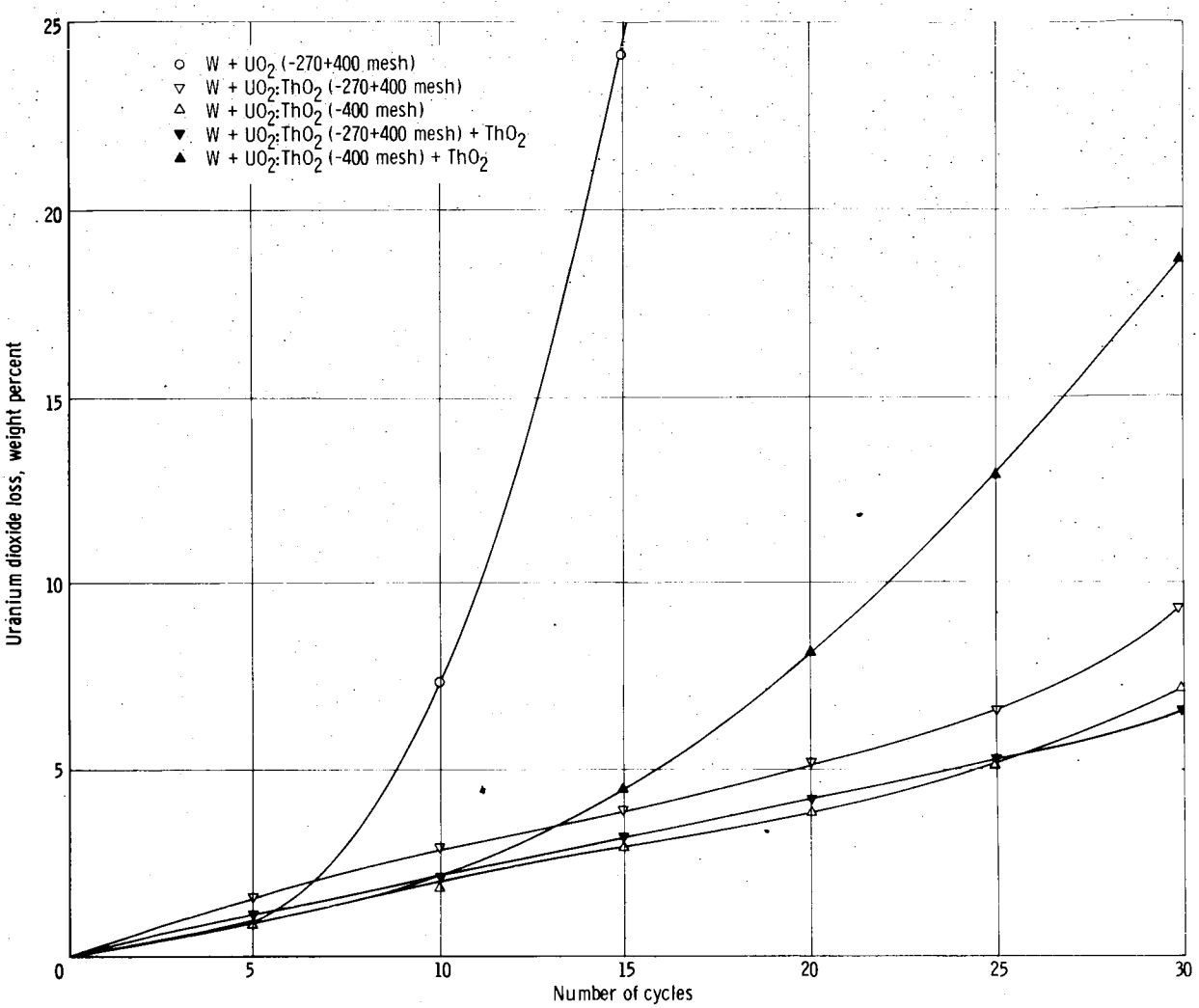
Weight-Loss Determinations

The weight-loss data exhibited a rapid rate of loss during the first two or three cy-



(b) Composites containing zirconium dioxide.

Figure 4. - Continued.



(c) Composites containing thorium dioxide.

Figure 4. - Concluded.

cles and then decreased to a substantially linear rate. This initial loss can be attributed to direct vaporization of oxide particles exposed at the unclad edges. When the data were plotted, these initial portions of the curves were eliminated by extrapolating the substantially linear curves to zero cycles. This procedure permitted these linear portions of the curves to be directly comparable.

The fuel loss was calculated from the known original weight percent of contained oxide and from the measured total weight losses. Vaporization loss of tungsten under these conditions is shown in reference 1 to be insignificant compared with fuel loss.

The oxide fuel loss observed as a function of number of cycles is shown in figure 4. In the discussion, the composites without additional ThO_2 in the matrix will be designated W + UO_2:M and those with thoria, W + UO_2:M + ThO_2. The fuel-retention properties of the composites under the conditions investigated were improved by the solid-solution

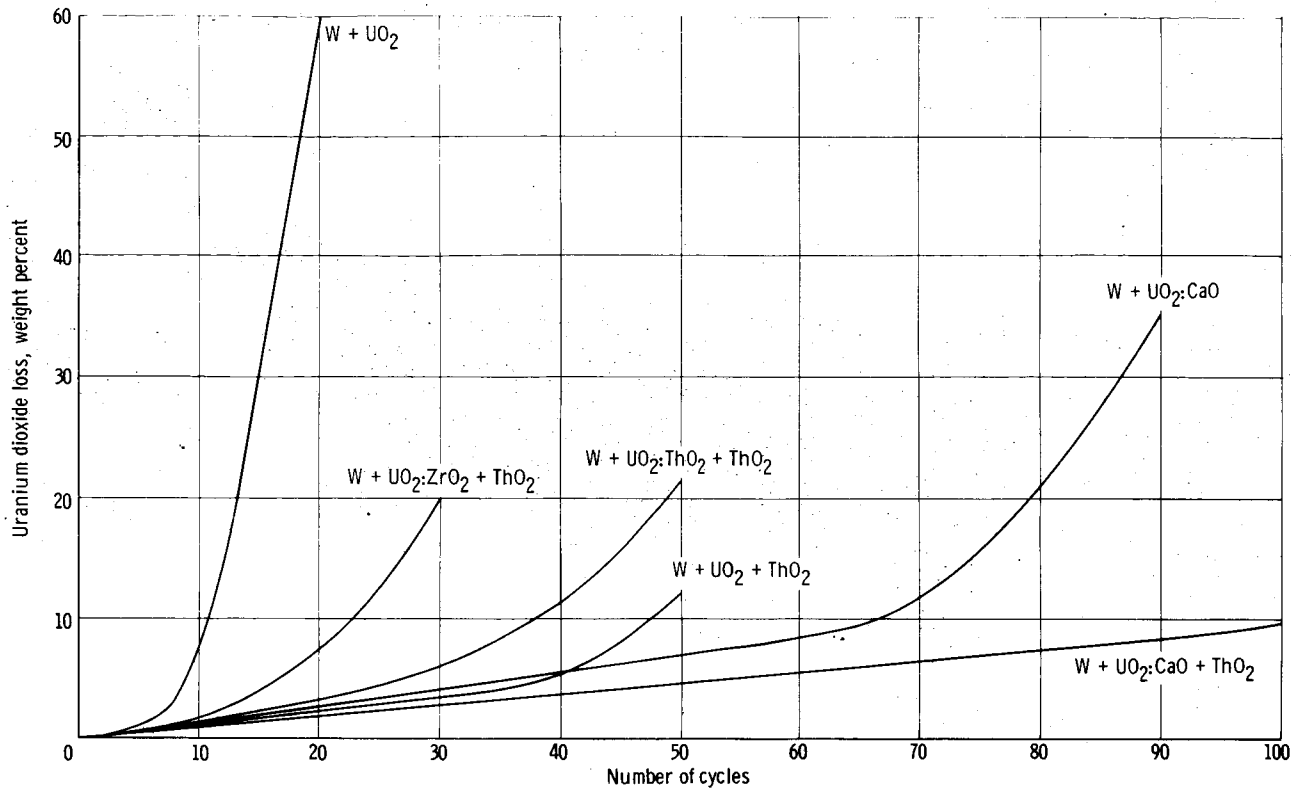


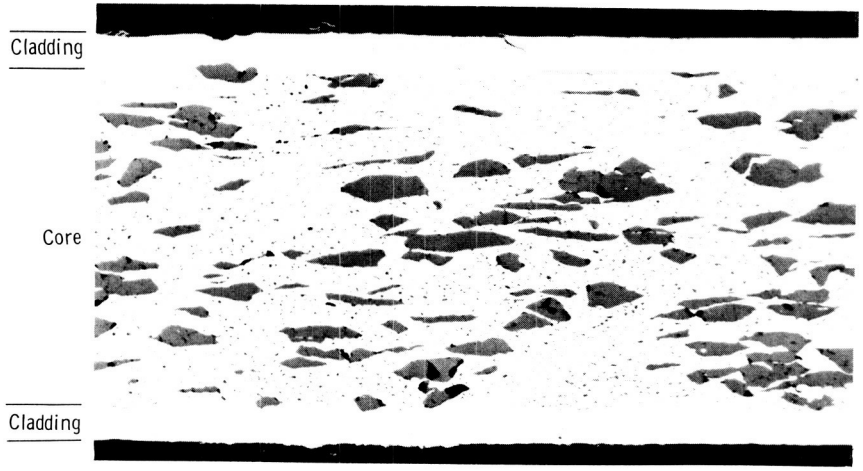
Figure 5. - Effect of solid-solution additives and thorium dioxide additions to matrix on thermal stability of tungsten - uranium dioxide composites.

additions. The W + UO_2:CaO composites were clearly superior to the W + UO_2:ZrO_2 or the W + UO_2:ThO_2 composites with respect to fuel loss. The presence of ThO_2 in the matrix had a smaller effect on fuel-retention properties of the composites than did the solid-solution additives. The effect of particle size was also comparatively small.

The effect of ThO_2 in the matrix becomes quite significant when observed over the larger number of cycles illustrated in figure 5. While the effect of ThO_2 in the matrix is not so pronounced as the effect of solid-solution CaO additions, the CaO and ThO_2 effects are apparently additive. The W + UO_2 composite lost 5 weight percent oxide in just nine cycles, the W + UO_2:ThO_2 + ThO_2 in 28 cycles, the W + UO_2:CaO in 40 cycles, and the W + UO_2:CaO + ThO_2 in 56 cycles. This latter number corresponds to almost 10 hours at 2500° C. Even after 100 cycles, the W + UO_2:CaO + ThO_2 composite exhibited a weight loss of less than 10 weight percent, which is significantly less than that of any other composite.

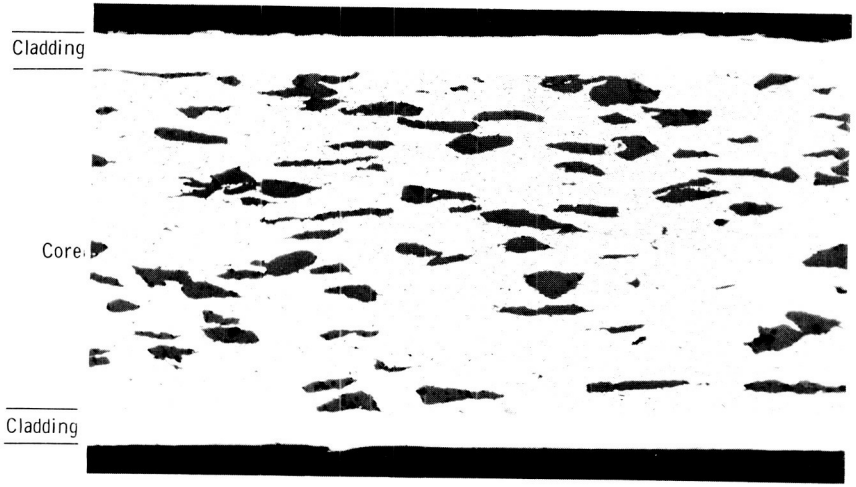
Microstructures

All the solid-solution UO_2 composites before cycling appeared similar to one another. Figures 6(a) and (b) are the photomicrographs of the W + UO_2:CaO composites

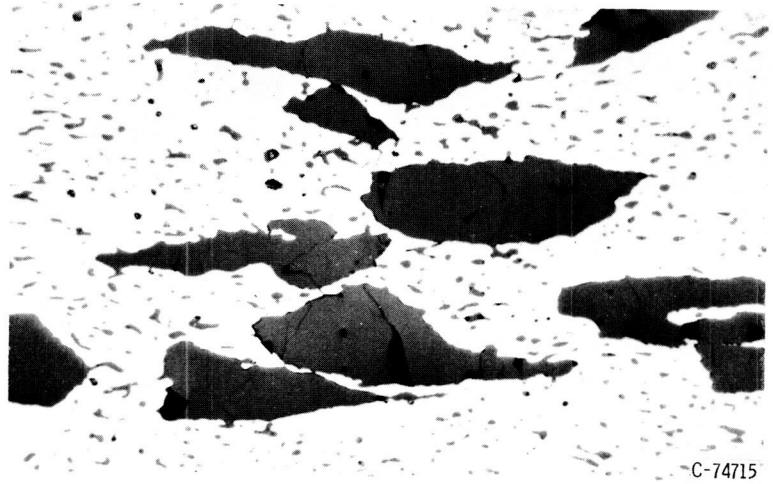


(a) Without thorium dioxide in matrix. X100.

(b) Without thorium dioxide in matrix. X500.

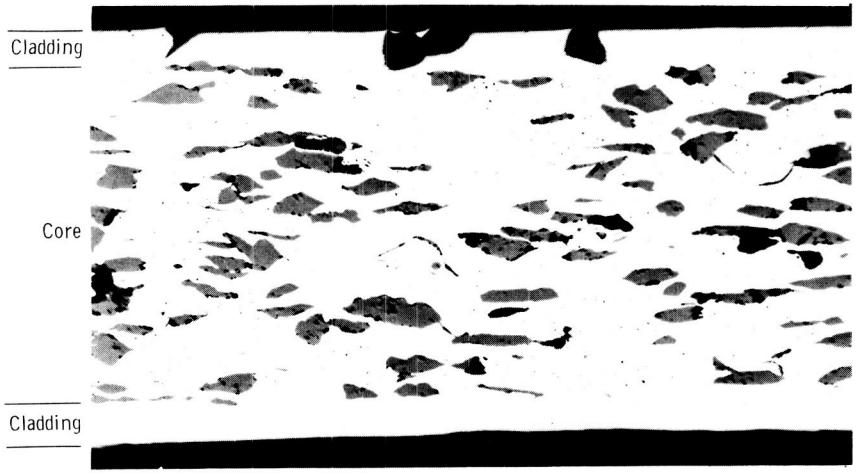


(c) With thorium dioxide in matrix. X100.



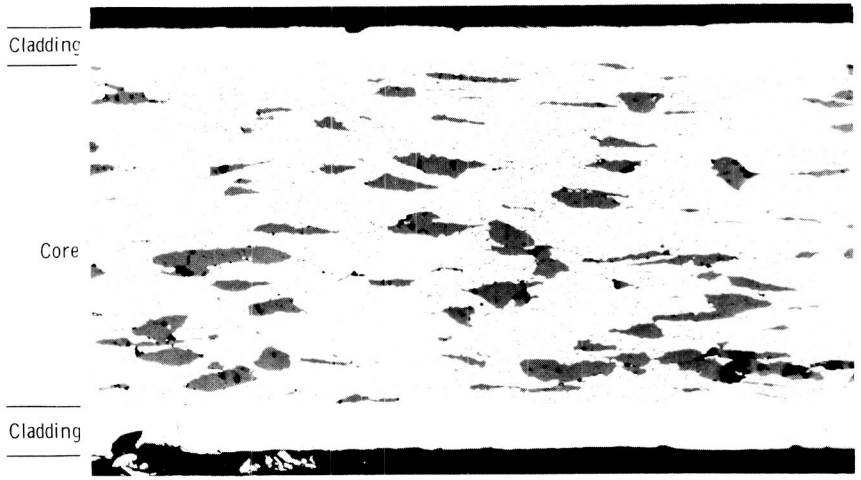
(d) With thorium dioxide in matrix. X500.

Figure 6. - Unetched cross section of tungsten - uranium dioxide - calcium oxide composites before cycling.

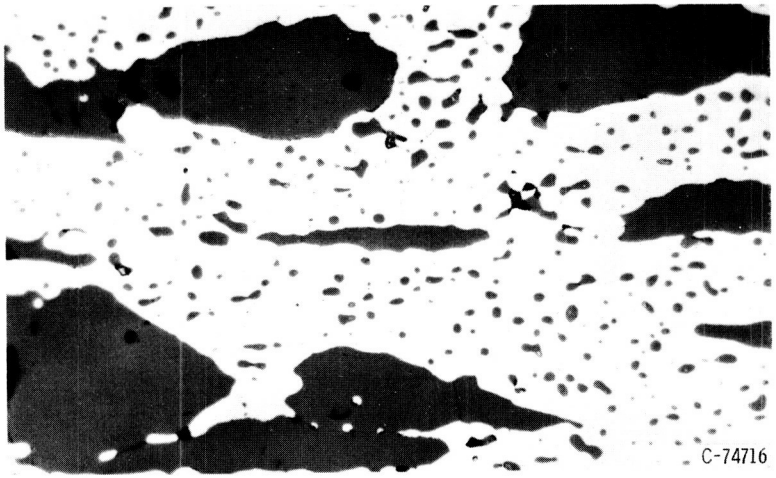


(a) Without thorium dioxide in matrix. X100.

(b) Without thorium dioxide in matrix. X500.

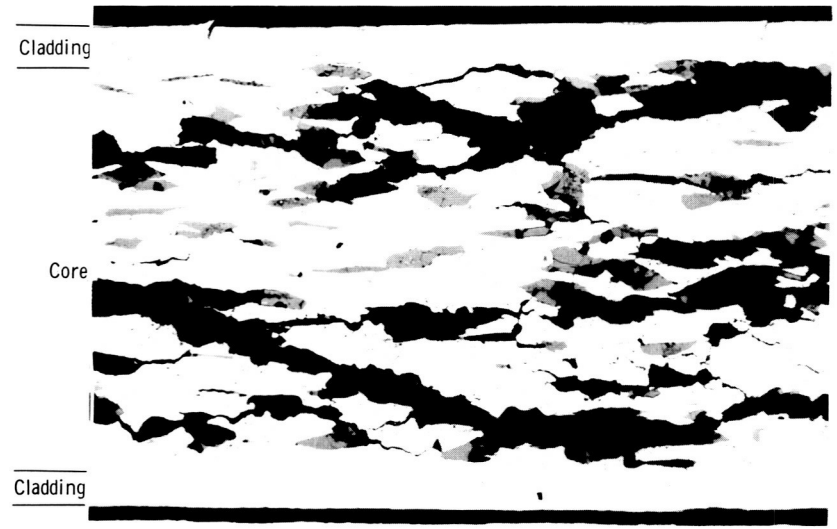


(c) With thorium dioxide in matrix. X100.

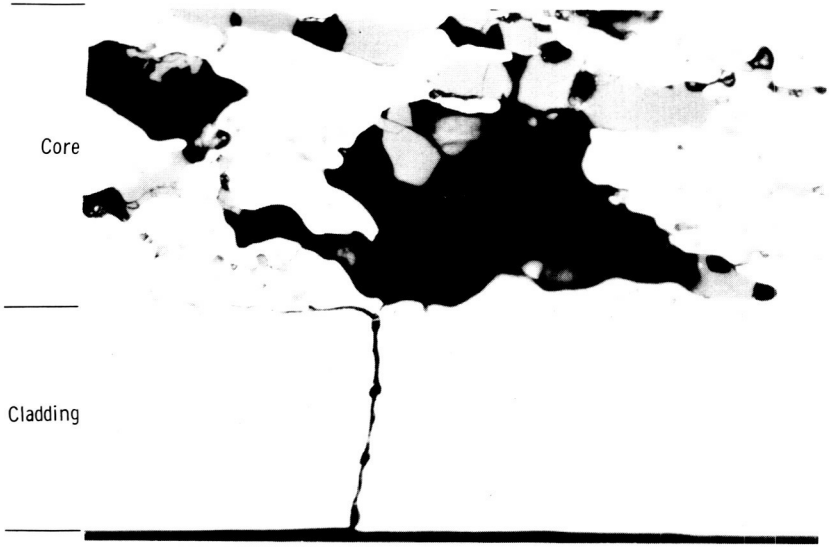


(d) With thorium dioxide in matrix. X500.

Figure 7. - Unetched cross section of tungsten - uranium oxide - calcium oxide composites after 25 cycles.

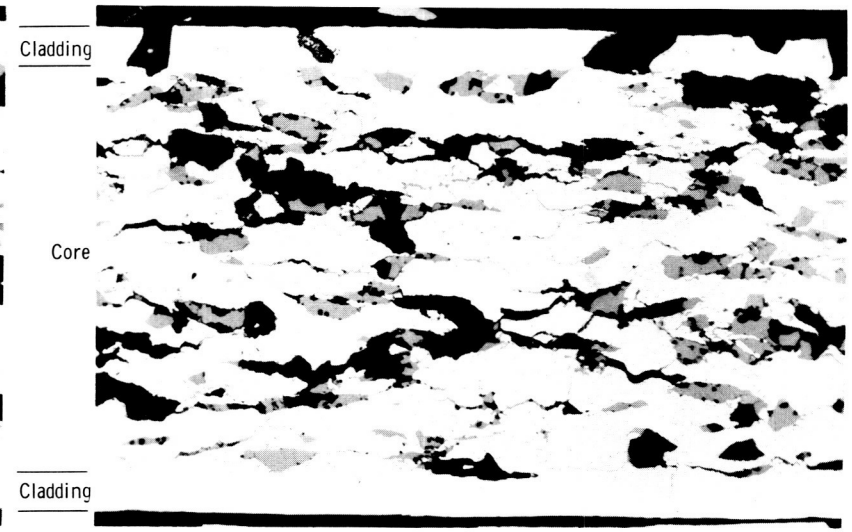


(a) X100.

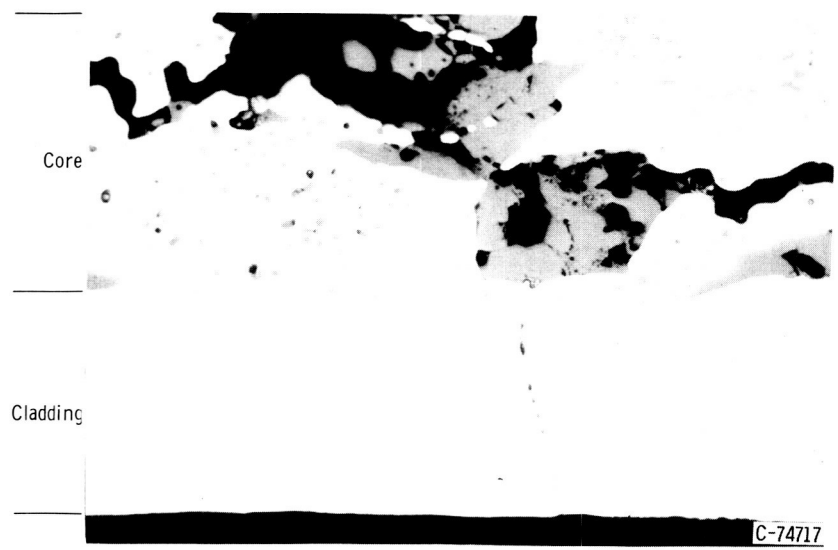


(b) X500.

Figure 8. - Unetched cross section of tungsten - uranium dioxide - zirconium dioxide - thorium dioxide composites after 30 cycles.



(a) X100.



(b) X500.

Figure 9. - Unetched cross section of tungsten - uranium dioxide - thorium dioxide composites after 30 cycles.

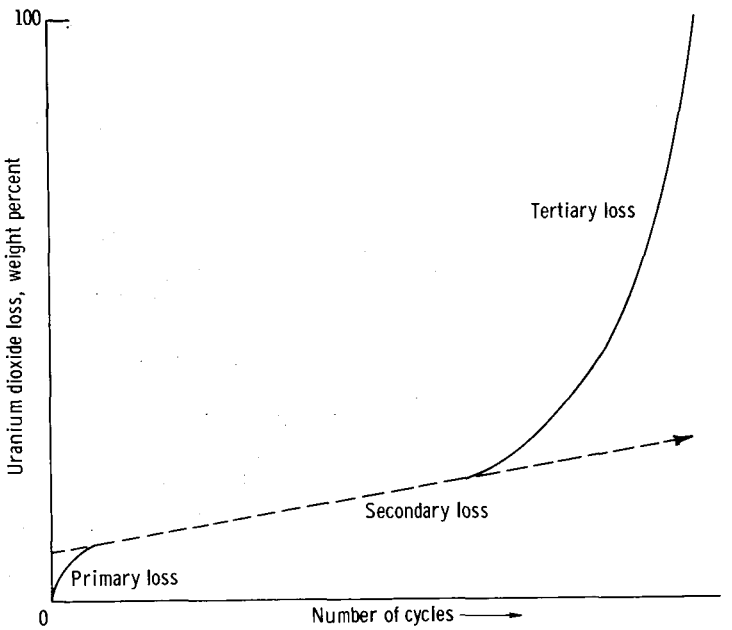


Figure 10. - Schematic representation of weight-loss curve for uranium dioxide in tungsten - uranium dioxide composites.

fabricated with the -270+400 mesh powder. Figures 6(c) and (d) illustrate the same material but with ThO_2 in the matrix. These photomicrographs are also representative of the ZrO_2-containing and the ThO_2-containing composites prior to cycling.

After 25 cycles, the appearance of each of the W + UO_2:CaO composites was almost identical to its appearance before cycling, as shown in a comparison of the photomicrographs of figure 7 with those of figure 6.

The amount of oxide absent from the microstructures of the W + UO_2:ZrO_2 and the W + UO_2:ThO_2 composites after 30 cycles (figs. 8 and 9) is greater than can be accounted for by weight-loss measurements. These composites could not be polished because of the pullout of the oxide. A portion of the apparent loss was thus due to the polishing process.

DISCUSSION

General Characteristics of Weight-Loss Curves

Figure 10 is a schematic representation of a weight-loss curve for W + UO_2 composites. Various portions of the curve are designated primary, secondary, and tertiary stages of weight loss. In all stages, the weight loss is by vaporization. The rate controlling step, however, is different in each process.

Primary loss is caused by vaporization of oxide particles that are exposed to the

unclad edges of the composite. This process is usually completed in two or three cycles. Because it is not dependent so much on the properties of the oxide as on the unclad surface area and number of oxide particles exposed to the surface, this portion of the loss curves of figures 4 and 5 (pp. 6 to 9) was eliminated as previously described. Primary weight loss never exceeded 4 percent and in most cases did not exceed 2 percent.

The secondary loss can be attributed to diffusion of oxide through grain boundaries or perhaps microcracks in the matrix and subsequent vaporization at the surface of the composite. This rate of weight loss would not be expected to change abruptly and might even be expected to decrease with increasing time at temperature because as the particles nearest the surface are consumed, transport time becomes progressively longer. The rate of vaporization will affect only the slope of the secondary curve, and if no other mechanism of weight loss is initiated, this curve should remain substantially linear until all the fuel is lost. This behavior, of course, does not occur. The length of the secondary curve is limited by the onset of the tertiary stage of weight loss. Figure 5 (p. 9) shows that the secondary curve is shortest for UO_2 without additives and increases in length with the addition of solid-solution and matrix oxides. The usefulness of the various composites examined is apparently dependent not only on the vaporization rate, that is, the slope of the secondary curve, but probably even more on its length. With the onset of the tertiary stage of weight loss, failure occurs rapidly.

Tertiary loss, characterized by a rapid increase in rate of weight loss, is probably the result of rupture of the matrix, which causes a rapid oxide loss by vaporization through macrocracks. The mechanism by which this catastrophic failure occurs is little understood, but sufficient knowledge has been accumulated that reasonable hypotheses can be made.

Hypothesized Mechanism Leading to Tertiary Loss

The observed formation of metallic uranium is thought to be caused by the formation of oxygen-deficient UO_2 at elevated temperatures and its subsequent disproportionation at lower temperatures (ref. 1). The loss of oxygen to form substoichiometric uranium dioxide (UO_{2-x}) can be represented as

$$UO_2 \rightarrow UO_{2-x} + xO \tag{1}$$

The rate of this reaction will depend on the rate at which the oxygen leaves the metal-oxide interface and thus on the oxygen concentration gradient between the metal-oxide interface and the surface of the composite. Grain boundaries in the tungsten matrix would probably serve as preferred migration channels for the oxygen.

[redacted]

On cooling, the oxygen-deficient UO_2 would be expected to disproportionate to uranium metal and UO_2.

$$2UO_{2-x} \rightarrow (2 - x)UO_2 + xU \qquad (2)$$

On subsequent heating, the uranium probably migrates along grain boundaries away from the oxide grains. At a sufficiently high temperature, the oxygen liberated by reaction (1) could react with the grain boundary uranium to form oxygen-deficient uranium dioxide UO_{2-x}. The volume change accompanying the formation of the oxide at grain boundaries would induce stresses in the matrix. With each subsequent heating period further migration would occur and during each cooling cycle additional uranium would be formed. At some stress level, physical rupture of the matrix would occur, which would expose oxide particles to the atmosphere with subsequent catastrophic fuel loss.

If it were possible to delay the onset of reactions (1) and (2) or to decrease their rates, the useful life of W + UO_2 composites could be greatly lengthened. The effect of solid-solution additives is thought to be primarily on the rate of reaction (1). Figure 5 (p. 9) shows that solid-solution additives have an insignificant effect on the slope of the secondary stage of weight loss.

Hypothesized Mechanism of Stabilization by Additives

The solid-solution additions of CaO, ZrO_2, and ThO_2 to UO_2 will alter the thermodynamic properties of this material. Calcium oxide would be expected to have a more pronounced effect on the thermodynamic properties than the other additions, since this oxide forms a vacancy defect structure with UO_2. If it is assumed that the UO_2:CaO did not appreciably oxidize, then the material tested, with approximately 10 atomic percent CaO, will have 5 percent of its oxygen lattice sites vacant. This oxygen deficiency would be expected to lower the oxygen activity of the UO_2 and thus to decrease the rate of oxygen loss.

Although solid-solution additions of ZrO_2 and ThO_2 also decreased the rate of fuel loss, their effects were not so significant as that of CaO. Thorium dioxide probably increased the thermal stability of the UO_2 lattice, as is suggested by the increase in the melting temperature of UO_2 by ThO_2 additions. Zirconium dioxide had the least effect on weight loss.

Thorium dioxide has a stabilizing effect on the UO_2 lattice under the testing conditions cited, probably by virtue of its great thermodynamic stability. Calcium oxide also has a stabilizing effect on the UO_2 lattice, probably by forming a vacancy defect structure with UO_2. Because of these stabilizing effects, it is conceivable that by inducing a

[redacted]

defect structure in ThO_2-stabilized UO_2 (e.g., by the addition of CaO, Y_2O_3, or Nd_2O_3) the additional stabilization would be greater than that achieved by either mechanism operating alone in the UO_2 lattice.

The effect of the mechanical properties of the oxides on the thermal stability of the composites under cyclic heating may be as important as the thermodynamic stability of the oxides. Kramers and Smith (ref. 7, p. 603) examined the mechanical properties of binary oxides with solid-solution ranges and showed that these compounds possess their highest hardness at the stoichiometric composition, which apparently indicates that a defect structure is more readily deformed than one possessing no defects. Hardness tests on the oxides investigated confirm this observation (table II, p. 4).

It is conceivable that the oxide phase of a W + UO_2 composite will crack during the rapid cooling period of a thermal cycle and thus cause an increase in the surface area of the oxide particles, which would promote reaction (1). If the lower hardness of the UO_2:CaO and the UO_2:ThO_2 indicates greater deformability than the UO_2, then thermal stresses are more likely to be relieved by deformation than by cracking for these solid solutions, as contrasted with UO_2.

On heating, the rate at which any cracks that did form in the oxide phase will heal will be greater for the UO_2:CaO than for the UO_2:ThO_2 solid solution because sintering rates are greatly enhanced by defect structures (ref. 8, p. 565). Compared with UO_2 solid solutions without a defect structure, the CaO-containing oxide will thus be less susceptible to cracking on cooling, and cracks that do form will be more quickly healed on heating.

Hypothesized Environmental Influence

If the proposed model of tertiary weight loss has merit, predicting the effect of environment on the initiation of tertiary loss should be possible. Because the rate of reaction (1) is dependent on the rate at which oxygen leaves the oxide-metal interface and thus on the oxygen gradient between this interface and the surface, the effect of environment would primarily be on the rate at which oxygen leaves the surface. A vacuum environment would promote the loss of oxygen by continuously maintaining the oxygen activity in the atmosphere below the level in the matrix. While an inert gas atmosphere would also be expected to promote oxygen loss by lowering the oxygen activity in the system, the kinetic effect of the total gas pressure would tend to decrease the rate of outgassing. If the products are assumed to be swept away by the gas stream, hydrogen would have the greatest effect on promoting oxygen loss by direct reaction on the surface to decrease the oxygen concentration in the matrix.

Thus, according to the model, an inert gas such as helium would have the greatest

effect in delaying the initiation of the tertiary stage of weight loss, whereas hydrogen would have the greatest tendency to expedite it.

In addition, the light helium atom or hydrogen molecule at 1 atmosphere would have almost the same effect as a vacuum on the rate of vaporization of UO_2 to form high-molecular-weight gaseous uranium-oxygen compounds. This behavior was observed by Gedwill, Sikora, and Caves (ref. 1). They found that environment had virtually no effect on the secondary stage of weight loss, but, as hypothesized herein, that environment did significantly affect the initiation of the tertiary stage.

SUMMARY OF RESULTS

In an investigation of the effect of additives on the thermal stability of tungsten - uranium dioxide composites, the following results were obtained:

1. The solid-solution addition of calcium oxide, zirconium dioxide, and thorium dioxide to uranium dioxide improved the fuel-retention properties of tungsten - uranium dioxide composites under cyclic heating to 2500° C in flowing hydrogen.

2. The improved stability of the uranium dioxide by the addition of calcium oxide was appreciably better than that shown by the other solid-solution additives.

3. The effect of thorium dioxide additions to the matrix on the fuel-retention properties was not so pronounced as the effect of calcium oxide in solid solution; however, their effects were generally additive.

4. A model based on the reduction and disproportionation of uranium dioxide was hypothesized to describe the mechanism of fuel loss from tungsten - uranium dioxide composites and their subsequent failure.

5. The effect of solid-solution additions of calcium oxide, zirconium dioxide, and thorium dioxide and matrix additions of thorium dioxide on the fuel-retention behavior of tungsten - uranium dioxide composites was hypothesized according to the preceding model.

6. The effect of hydrogen, helium, and vacuum environments on the fuel-retention behavior of tungsten - uranium dioxide composites is also discussed with reference to the hypothesized model.

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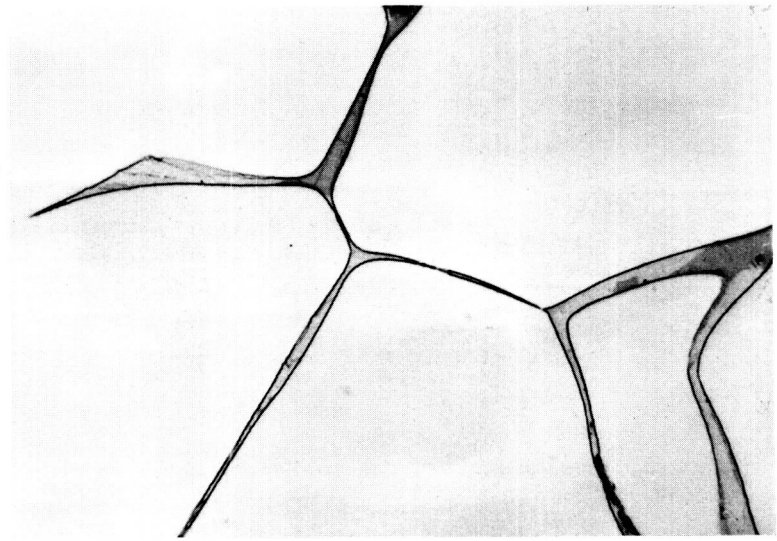
APPENDIX - SOLID-SOLUTION MICROSTRUCTURES

Figure 11(a) illustrates the microstructure of the as-sintered UO_2 compact. The bright phase has not been identified in this specimen but is apparently metallic. The continuous phase is probably U_4O_9. The ceramic-grade powder (O/U = 2.2) has the structure of U_4O_9 above 1000° C (ref. 2, p. 237) and probably also at the sintering temperature. If the sintering treatment did not remove all the combined oxygen in excess of an O/U of 2, then U_4O_9 could form from UO_2 under the slow cooling (10° C/min) experienced by the compact, since this phase coexists with UO_2 between values of O/U of 2 and 2.25. If the O/U of the compact is above 2, however, then the metallic phase of figure 11(a) could not be free uranium. The bright phase in figure 11(c), which has the same appearance as the bright phase in figure 11(a), has been identified as tungsten by electron-probe microanalysis. It is thus reasonable to assume that both specimens picked up tungsten from the crucible.

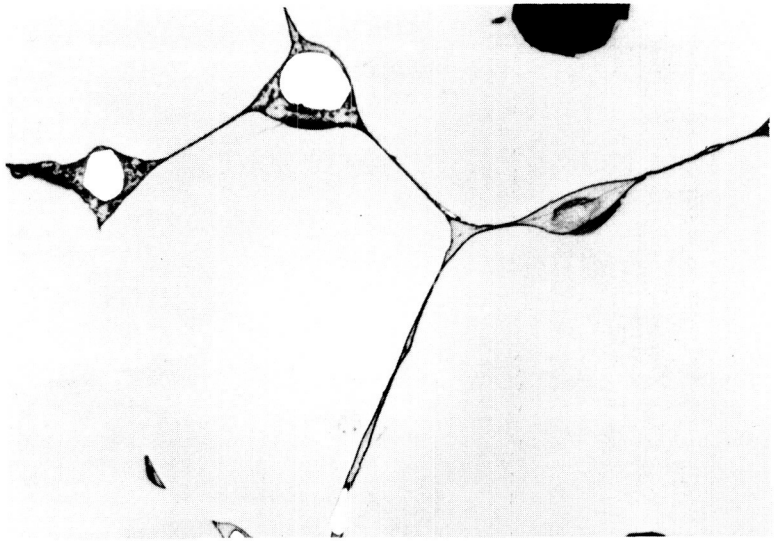
Both the UO_2:ZrO_2 and the UO_2:ThO_2 solid solutions (figs. 11(b) and (c)) exhibited a continuous grain boundary phase. Apparently, complete interdiffusion did not occur during the sintering cycle described. Although a single phase was not formed, the powder patterns for these materials showed only an expanded or a contracted UO_2 lattice, with no ZrO_2 or ThO_2 lines discernible.

Because of the presence of a liquid phase during sintering, diffusion was rapid enough in the UO_2:CaO compact that complete solid solution occurred in the allotted time at temperature, as illustrated by figure 11(d), in which a grain boundary phase is absent.

(a) Uranium dioxide.



(b) Uranium dioxide - 10-atomic-percent zirconium dioxide solid solution.



(c) Uranium dioxide - 10-atomic-percent thorium dioxide solid solution.

(d) Uranium dioxide - 10-atomic-percent calcium oxide solid solution.

Figure 11. - Unetched as-sintered microstructures. X500.

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